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HIGH RESOLUTION ELECTRON ENERGY LOSS STUDIES OF SURFACE VIBRATIONS

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Abstract

New experimental investigations of surface vibrational properties of materials with high-resolution electron energy loss spectroscopy (EELS) are reported. This document summarizes recent progress on surface phonon dispersion measurements on copper (100), copper (111), aluminum (100) surfaces and ultrathin epitaxial films of nickel and cobalt on copper (100). Measurements on copper and aluminum surfaces show modest changes in surface force constants compared with bulk values and are consistent with first principles lattice dynamics calculations. Measurements on the ultrathin magnetic film systems have revealed new modes associated with vibrations localized in the film.

A. Summary of Research

In this section we will outline the major accomplishments of our experimental program on surface phonon measurements which began in 1984. We shall place the main emphasis on progress made during the current funding cycle of November, 1987 to present. The materials we have studied include the following:

- clean copper (100)
- copper (100) with adsorbed nitrogen, oxygen, and sulfur overlayers
- clean copper (111)
- clean aluminum (100)
- ultrathin films of nickel on copper (100) [denoted as Ni/Cu(100)]
- ultrathin films of cobalt on copper (100) [Co/Cu(100)]
- adsorbate systems O/Ni/Cu(100) and O/Co/Cu(100)
- semiconductor systems (preliminary)

Below we discuss the salient results for several of these systems.

a. Cu(100)

In 1985-86 we reported our initial experimental results for the Rayleigh (S_4) phonon dispersion of clean Cu(100).[1-2] We were able to report for the first time the achievement of one to two orders of magnitude higher experimental phonon loss intensities than was previously obtained on similar systems. For example, the measured intensities for the S_4 phonon loss on Cu(100) were 250 cps

near the $\bar{X}$ point as compared to 5 cps in the earlier work on Ni(100).[3] It was possible to conclude that this was a real instrumental improvement rather than a cross section effect by comparing theoretical calculations made on the two materials under the appropriate scattering conditions.[4] Since that time other research groups have incorporated our concept of a dual stage monochromator[5] of cylindrical or hemispherical design consisting of a premonochromator with appropriate coupling lens system to a main (high resolution) stage followed by a multielement zoom lens system in order to achieve relatively high signal levels.

The measured S_4 phonon dispersion from $\bar{\Gamma}$ to $\bar{X}$ on Cu(100) could be fit by a surface lattice dynamics model in which the force constant k_{12} between the first and second copper layers was increased 16% from the bulk value.[1] Qualitatively, the increase in force constant k_{12} is consistent with a small geometric contraction of about 1% reported by Davis and Noonan in their LEED analysis of Cu(100).[6]

An important aspect of our observations on Cu(100) was the measurement and subsequent analysis of bulk phonon excitations. Whereas data we obtained at 81 eV primary energy showed only a strong Rayleigh mode (S_4) cross-section we noted that 110 eV data exhibited also a prominent shoulder likely caused by bulk phonon excitations. Such "resonance" modes are due to certain bulk phonons which reflect from the surface with a large amplitude resonance response. Detailed analysis by Tong and Xu using a full

multiple-scattering theory confirmed the importance of such resonance modes. We reported these results in 1986 in the first detailed cross section analysis of both surface and bulk phonon contributions to the measured EELS spectra.[1] Similar cross section analysis of Ni(100) phonon data emphasizing both bulk and surface contributions were subsequently reported by Hall and Mills.[7] Resonance modes, in addition to pure surface modes, provide an important source of information in elucidating the surface lattice dynamics.

b. Cu(111)

We devoted a major effort to determining the nature of surface phonons on the Cu(111) surface. In addition to our experimental measurements we collaborated with D.L. Mills and Burl M. Hall at the University of California at Irvine in a theoretical analysis of EELS scattering intensities and the Cu(111) lattice dynamics. Details of our investigations have been reported in Refs. 8-10.

Our studies were partially motivated by high-resolution inelastic He scattering measurements due to Toennies and co-workers which raised exciting issues regarding surface phonon dispersion on the (111) surfaces of the noble metals Cu, Ag and Au.[11] In particular, a new longitudinal resonance (LR) detected above the Rayleigh mode (S_1) was interpreted by Bortolani et. al. in terms of a marked 50% weakening of the lateral force constants in the uppermost surface layer for Ag(111).[12] A softening of 50% for Cu(111) was suggested as well, whereas a similar explanation for

Au(111) requires a remarkable 70% reduction. These results were certainly surprising in view of the close-packed nature of the (111) surfaces and the lack of significant geometric reconstruction or relaxation for Cu(111) and Ag(111), although Au(111) exhibits a type of reconstruction.

The He scattering measurements noted above were restricted to the lower-frequency portion of the dispersion curves and, importantly did not probe the surface modes which are predicted to lie in gaps in the bulk phonon bands near the surface Brillouin-zone (SBZ) boundaries. Such gaps modes are quite sensitive, in general, to changes in the surface force constants and motivated our EELS measurements on Cu(111). In Ref. 8 we reported the first experimental determination of the S_2 mode frequency near $\bar{M}$ in the SBZ, for Cu(111). We also observed the S_1 and LR modes out to $\bar{M}$, thus extending the earlier He scattering measurements to the SBZ boundary. We also identified other surface resonances at higher frequencies for the first time.

Our most important finding concerned the gap mode S_2: the 210 cm^{-1} frequency of this mode, i.e., distinctly above midgap, appeared to rule out the 50-70% softening models and indeed was most consistent with an approximate 15% softening. Furthermore, we found that detailed cross-section analysis, based upon multiple scattering of the electrons, was consistent with a modest (15%) softening model and satisfactorily explained the basic intensity features associated with the Rayleigh, longitudinal resonances, and gap modes. Our results thus stood in sharp contrast to the model

advanced by Bortolani and co-workers which purported to explain the surface lattice dynamics of the Cu, Ag, and Au(111) surfaces in terms of dramatic intralayer force constant softening.

Following our experimental work and simple force constant analysis, more recent lattice dynamics calculations based on the embedded-atom method (EAM) were reported for Cu(111) and Ag(111) by Nelson et. al.[13] Their EAM calculations, which incorporate many-body interactions into the expression for the total energy, are consistent with our findings of 15% change in the surface force constants for Cu(111).

c. Al(100)

In 1987 we reported the first experimental measurements of the Rayleigh surface mode dispersion for the aluminum (100) surface.[14] Excellent agreement was found between our experimental results and the theoretical first-principles calculations performed by Bohnen and Ho[15] for the phonon energy at $\bar{X}$. More recent first principles calculations using a density-response theory method by Equiluz et. al.[16] are also in substantial agreement with our data. The agreement found for the aluminum surface has served as a strong motivation to extend these first principles calculations to the case of transition metals.

d. Ultrathin Epitaxial Films

There has been recent keen interest in the properties of ultrathin epitaxial films of a few monolayers (ML) thickness. Iron

and cobalt, for example, may be grown in metastable fcc layers on a copper (001) substrate. The investigation of the magnetic behavior of such films has therefore been one such area of interest. Much of our work in the past two years has been devoted to a study of the vibrational properties of nickel and cobalt films (2-6 ML thick) on a copper (001) substrate. We have also examined the nature of oxygen adsorption on these films. Our early efforts involved developing methods in our laboratory to assure good epitaxial growth of highly-ordered films in a clean ultrahigh vacuum environment. In the case of nickel overlayers special care must be taken to avoid diffusion of nickel in copper. These problems were solved by careful design of the evaporation source and by restricting the substrate temperature during evaporation and post-evaporation substrate annealing. The integrity of the films was verified by low-energy electron diffraction, Auger electron spectroscopy and EELS.

Our first phonon measurements[17] on the Ni/Cu(001) system concerned the phonon dispersion from $\bar{\Gamma}$-$\bar{X}$ in the SBZ and were reported in 1989. These measurements were partly motivated by lattice dynamical calculations by Tong et. al.[18] dealing with the general vibrational properties of epitaxial films of Cu on Ni(001). These authors reported the nature of the surface phonon dispersion as a function of overlayer thickness based on a nearest-neighbor central force lattice dynamical slab model. Novel features predicted in these calculations include the existence of so-called film modes (F_i) which correspond to vibrational modes localized

primarily in the overlayer film. In our experiments we reported the first observation of such modes, which are expected to be a general feature of phonon dispersion in ultrathin films. The film modes observed lay in substantially the same frequency region above the copper bulk phonon band edge in agreement with the calculations of Tong et. al.

In addition to the film modes, we also reported the Rayleigh phonon mode (S_4) dispersion from $\bar{\Gamma}$ to $\bar{X}$ for film thicknesses of 2-6 ML. The Rayleigh mode frequency for these films is found to be substantially higher than the clean copper S_4 mode but lower than the case for clean nickel.

We have also reported the Rayleigh phonon dispersion for ultrathin films of cobalt on Cu(001).[19] This data indicates a marked flattening of the dispersion curve near the SBZ boundary along $\bar{\Gamma}$ to $\bar{X}$, suggestive of surface stress in the films.

Our work is continuing on these interesting ultrathin film systems. We have obtained additional data on the phonon dispersion along $\bar{\Gamma}$ - $\bar{M}$ in order to better define the force constant models that are consistent with all the data.

e. Adsorbate systems O/Ni/Cu(001) and O/Co/Cu(001)

We have studied the Rayleigh phonon dispersion for ultrathin nickel films on a Cu(001) substrate which have been exposed to oxygen. The oxygen atoms form well-ordered c(2x2) overlayers on the nickel films. When exposed to oxygen the Rayleigh phonon

frequency at the zone boundary ($\bar{X}$) drops 20-35 cm^{-1}, depending on the nickel film thickness. We also find that the Rayleigh phonon frequency in the presence of oxygen varies systematically with nickel film thickness, implying changes in the electronic structure of the films with oxygen exposure.

In the case of O/Co/Cu(001) the dipole-active optical modes associated with oxygen-cobalt interactions show interesting changes as a function of Co film thickness. The position and relative intensity of these modes changes rather dramatically in the region between 2 and 3 ML of cobalt thickness. This is consistent with clustering of the cobalt for film thickness $\bar{<}$ 2ML followed by layer by layer growth after 3ML.

In both of these overlayer systems we have had rather complete data in hand for some time. However, we are awaiting detailed theoretical analysis before publishing these results. This analysis has been delayed until the analysis of the clean film systems discussed above is completed.

f. Semiconductor surfaces

We have completed construction of a new experimental facility for surface phonon measurements on semiconductor surfaces. Construction commenced in 1988 with funding support of 90K in equipment monies from Indiana University. This facility consists of an ion-pumped ultrahigh vacuum system with a rotatable electron energy loss spectrometer and a sample manipulator providing both

polar and azimuthal sample rotation. The system is also equipped for low-energy electron diffraction, Auger spectroscopy and metal evaporation source. Initial spectrometer tests on the system were completed in 1989, but problems associated with the commercial sample holder had resulted in several delays. The facility is now operational and initial studies on the Al/Si(111) system are underway.

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